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IMPACT SENSITIVITY OF LIQUID OZONE

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TECHNICAL MEMORANDUM X-88

IMPACT SENSITIVITY OF LIQUID OZONE*

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SUMMARY

The impact sensitivity of liquid ozone and ozone mixtures was studied at temperatures near -196° C with a drop-weight impact tester. The systems tested were binary mixtures (9.1 mole percent) of carbon tetrafluoride, oxygen bifluoride, fluorine, carbon monoxide, oxygen, and ethane in liquid ozone. The results did not confirm suggestions that (1) the presence of a Freon, carbon tetrafluoride (CF_4), or (2) the presence of strong oxidants, fluorine (F_2) and oxygen bifluoride (OF_2), to oxidize impurities, should stabilize ozone. These substances had little effect on the impact sensitivity. Carbon monoxide also showed only a slight effect. Some enhancement of the sensitivity was caused by ethane. Only oxygen had an appreciable desensitizing effect.

INTRODUCTION

Attempts have been made in recent years to reduce the shock sensitivity of ozone so that it might be safely handled in rocket applications. Mixtures containing as little as 50 percent ozone in oxygen will propagate extremely destructive Chapman-Jouguet type detonations. Even mixtures of as little as 35 percent ozone in oxygen can explode destructively when suitably initiated (ref. 1).

Among the methods that have been suggested for reducing the shock sensitivity of liquid ozone is that of adding small concentrations of other substances to the ozone (ref. 2, pp. 129-130). For example, it has been suggested that small amounts of Freons reduce the sensitivity of ozone appreciably (refs. 2, pp. 129-130, 3, and 4).

It has also been suggested that the shock sensitivity of ozone is due primarily to the presence of small amounts of easily oxidizable impurities, for example, unsaturated hydrocarbons (refs. 5 and 6). If this suggestion is correct, the addition of very reactive oxidants to ozone could be expected to either bring about immediate explosion or stabilize

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the ozone by removing these impurities. Both fluorine and oxygen bifluoride react much more readily with ordinary oxidizable substances than does ozone (refs. 2, p. 138, and 6) and might be expected to have this effect.

A study was therefore undertaken to investigate the effect of carbon tetrafluoride, oxygen bifluoride, and fluorine on the impact sensitivity of ozone. Also included in this study were mixtures of ozone with liquid oxygen and with two oxidizable substances, carbon monoxide and ethane. The impact sensitivities were measured with a drop-weight impact tester. In this tester a freely falling weight falls on a metal striker, causing it to strike the liquid which has been condensed in a cup.

No attempt was made to relate the drop height to the absolute energy required to cause an explosion. However, experimental conditions were carefully controlled so that the drop height might be considered a measure of the relative magnitude of the mechanical shock needed to cause an explosion.

APPARATUS

Drop-Weight Impact Apparatus

The drop-weight impact apparatus (fig. 1), a modification of a standard testing device (ref. 7), was designed to handle small quantities of liquids at low temperatures. It consisted primarily of a tester and a weight-dropping mechanism. The tester was composed of a casing, an anvil, a striker, and a cup; the pieces were made entirely of 304 stainless steel. The tester sat in an insulated metal container, which contained liquid nitrogen. A copper-constantan thermocouple was embedded in the anvil and indicated the temperature of the cup. A desired temperature could be obtained by varying the amount of liquid nitrogen in the container.

The anvil was made of solid stainless steel 2 inches in diameter. The casing had a 1/2-inch wall, the inside of which was sloped to allow any liquid condensed thereon to drain into the cup.

The striker moved through a hole in the top of the casing and was connected to the casing by a stainless-steel bellows, which permitted movement of the striker while maintaining a vacuum-tight seal.

Several configurations were considered in designing the cup and the striker. The conclusion reached was that a replaceable, spherical-shaped cup and striker would be best for obtaining reproducible results. Therefore, the striker was made with a replaceable tip. Several cups and striker tips were made in sets as nearly identical as possible. In each set the tip was machined to fit the cup. The striker tip screwed into the top of the striker, and the cup fitted into a place machined in the casing. With the apparatus assembled, the cup fitted firmly against the casing and anvil. With 1 atmosphere of pressure in the apparatus, the striker was 3/32 inch above the cup.

The weight, a 303.1 gram lead-filled iron pipe, was contained inside a brass guide tube. When dropped, it was guided so that it hit the center of the striker top. The weight was lifted by a solenoid and could be dropped from any height up to 60 centimeters.

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Apparatus Enclosure and Manifold

The entire apparatus was enclosed inside a steel box of 1/4-inch sides with 1/2-inch Lucite windows (not shown in fig. 1). The metal container and anvil were bolted to the bottom of the box. Liquid nitrogen was added to the container through a funnel in the top of the box. All valves were operated remotely. The tester was connected to a manifold (fig. 2), which was connected to a storage bulb, a measuring bulb of 56.3-milliliter capacity, a manometer, a helium cylinder, the cylinder containing the additive, and a vacuum pump. The mercury manometer was protected with sulfuric acid. Thus, mercury never came in contact with the system.

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PROCEDURE

Testing of Ozone

For each test 0.03 milliliter of liquid ozone was used. This quantity was obtained by putting a predetermined pressure (216 mm Hg) of ozone in the measuring bulb, which was maintained in an acetone - dry ice bath. It was then transferred to the impact tester where it was condensed and collected in the cup.

With the ozone in the cup, the system was pressurized to 1 atmosphere with helium. The valve to the impact apparatus was closed and the weight dropped. The weight was first dropped from a minimum height of 6 centimeters. It was then dropped from successively higher heights until an explosion occurred. The occurrence of an explosion was determined by the sound produced and the rise in pressure.

Preparation and Testing of Mixtures of Ozone

All of the gases were at least 99 percent pure, except ethane and carbon tetrafluoride, which were at least 95 percent pure. They were used without further purification.

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Ozone was first measured and transferred as before. The additive was then brought into the system, measured, and mixed with the ozone. The system was pressurized to 1 atmosphere with helium and the weight dropped as described previously.

Oxygen bifluoride, carbon tetrafluoride, and ethane were measured in the measuring bulb, using one-tenth the pressure used for ozone. This then gave, when the additive was mixed with the ozone, a 9.1-mole-percent solution. The liquids were mixed by dropping the weight several times from a height of 6 centimeters. Very few explosions ever occurred during mixing.

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The concentrations of the other three additives, carbon monoxide, oxygen, and fluorine, were determined from the vapor pressures of the mixtures. Excess gaseous additive was admitted to the system. A period of 10 to 20 minutes was then allowed for the additive to dissolve in the ozone. When the pressure in the system had become constant, the excess additive was pumped off until the vapor pressure of the mixture was that of a 9.1-mole-percent solution.

In testing the 100 percent ozone, several temperatures were used ranging from -175° to -196° C. The ozone - oxygen bifluoride mixture was tested within the range -190° to -195° C, while the ozone - carbon tetrafluoride and ozone-ethane mixtures were tested in the range -178° to -183° C. The ozone - carbon monoxide, ozone-oxygen, and ozone-fluorine mixtures were all tested at -195° C.

Each day, before and during the testing of a mixture, tests were run with 100 percent ozone. If the cup and striker were found to be damaged, as evidenced by a marked increase in sensitivity, the testing was discontinued and the cup and striker changed. The set was also changed every time a new mixture was tested.

Vapor Pressures of Mixtures

The vapor pressure of the ozone-oxygen mixture was obtained from previous data (ref. 8). The vapor pressures of the ozone - carbon monoxide and ozone-fluorine mixtures at -195° C were obtained in this study. A desired amount of ozone was condensed in a glass bulb immersed in liquid nitrogen. A known amount of additive was then introduced into the system and allowed to dissolve. The amount of additive remaining in the vapor phase was measured, and by difference the amount dissolved at that pressure was obtained. The results are shown in table I and figure 3.

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RESULTS AND DISCUSSION

The impact sensitivity results are recorded in table II as "explosion efficiency" (i.e., $\frac{\text{no. of explosions}}{\text{no. of impacts}} \times 100$) at a given height. The explosion efficiencies are for a minimum number of 20 drops at each height except where fewer drops indicated clearly what the result would be. These results are plotted in figure 4, which shows straight-line plots for the systems tested. In reality, these are probably sigmoid curves which approach a straight line in the region between 10 and 90 percent explosion efficiency (ref. 9). It is customary to use the height at which 50 percent explosion efficiency occurs as the index of the sensitivity of an explosive. This height is readily obtainable from the straight-line plots.

Table III gives the heights for the 50 percent explosion efficiency points for ozone and the mixtures of ozone. As can be seen, the oxygen-ozone system is considerably less sensitive to impact when compared with the other systems. The oxygen bifluoride - ozone and carbon tetrafluoride - ozone mixtures are slightly less sensitive to impact than is ozone. This small difference is attributed to the dilution of the ozone rather than to any positive inhibition on the part of the oxygen bifluoride or carbon tetrafluoride. The carbon monoxide - ozone and fluorine-ozone mixtures show approximately the same sensitivity as 100 percent ozone, implying a slight sensitization by these two additives. Some justification is found for this when it is considered that carbon monoxide reacts explosively with ozone at higher temperatures and that fluorine speeds the decomposition of ozone (ref. 10). However, it must be pointed out that the differences are small and not very significant. The ozone-ethane mixture shows a somewhat greater sensitivity than does ozone alone. This difference is attributed to an enhancement of the decomposition by reaction of ozone with the hydrocarbon.

The effect of temperature on the impact sensitivity of liquid ozone is shown in table IV. From this it is concluded that temperature has no effect on the sensitivity of the ozone in the range tested.

SUMMARY OF RESULTS

The following results were obtained during the impact sensitivity investigation of liquid ozone and ozone mixtures near -196° C:

1. A typical Freon, carbon tetrafluoride, was relatively ineffective in reducing the impact sensitivity of liquid ozone.

2. Strong and reactive oxidizing agents such as oxygen bifluoride and fluorine that might be expected to remove traces of unsaturated

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hydrocarbons from liquid ozone were relatively ineffective in reducing its impact sensitivity.

3. Of the various diluents tested, liquid oxygen was most effective in reducing the impact sensitivity of liquid ozone.

4. The addition of carbon monoxide to liquid ozone had little effect on the impact sensitivity.

5. Solutions containing a large amount of a saturated hydrocarbon (9 percent ethane) in liquid ozone were somewhat more impact sensitive than liquid ozone itself.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, July 6, 1959

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TABLE I. - VAPOR PRESSURES OF OZONE-FLUORINE AND OZONE - CARBON MONOXIDE MIXTURES AT -195° C

(a) Fluorine in ozone

Pressure, mm Hg	Fluorine, mole percent	Pressure, mm Hg	Fluorine, mole percent
23.6	1.0	245.3	40.9
37.0	2.5	252.1	48.9
69.3	5.2	264.9	52.1
94.5	8.0	259.5	61.0
119.1	11.6	269.7	64.1
137.0	14.0	262.6	68.2
149.9	16.1	273.7	71.2
165.0	17.8	265.3	73.4
196.3	22.3	277.2	75.9
204.7	27.4	280.3	79.3
219.9	27.9	280.7	94.5
241.2	39.4	284.7	100.0

(b) Carbon monoxide in ozone

Pressure, mm Hg	Carbon monoxide, mole percent	Pressure, mm Hg	Carbon monoxide, mole percent
35.4	0.5	344.5	26.4
76.6	2.0	373.9	37.5
79.9	2.0	382.0	43.5
100.8	2.8	392.0	51.5
106.6	3.6	400.8	56.1
134.7	5.3	402.3	68.2
149.7	5.9	404.8	78.0
153.5	6.8	405.0	66.3
158.3	6.1	407.4	76.5
187.7	9.1	412.9	84.6
211.5	10.9	418.9	88.2
223.6	11.7	423.7	90.5
266.8	16.2	429.6	93.0
270.4	16.7	460.2	100.0
290.4	17.2	459.9	100.0
341.2	26.6		

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TABLE II. - EXPLOSION EFFICIENCIES OF OZONE AND OZONE MIXTURES

[Additive, 9.1 mole percent.]

Height, cm	Additive						
	None	Oxygen	Carbon tetra-fluoride	Oxygen bifluoride	Carbon monoxide	Fluorine	Ethane
36		90.9					
32		45.0					
28		36.4					
24		----	[a]100.0	[a]100.0	[a]100.0		
21		19.0	------	------	------		
20	80.0	----	47.7	60.0	70.0	93.8	
16	57.7	0	15.0	15.0	50.0	60.0	[b]93.1
11	5.6	4.2	0	0	20.0	8.0	72.8
9	----	----	------	------	------	----	14.8
6	2.9	----	0	------	0	0	0

[a]10 Drops.
[b]15 Drops.

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TABLE III. - HEIGHTS OF 50 PERCENT EXPLOSION

EFFICIENCY OF OZONE AND OZONE MIXTURES

[Additive, 9.1 mole percent.]

Additive	Height, cm
Ethane	10.6
Fluorine	15.2
None (ozone)	15.8
Carbon monoxide	16.3
Oxygen bifluoride	19.2
Carbon tetrafluoride	19.6
Oxygen	33.9

TABLE IV. - EFFECT OF TEMPERATURE ON

IMPACT SENSITIVITY OF OZONE

Height, cm	Temperature, °C	Explosions, percent
11	-180	9
	-195	8
16	-180	46
	-195	57
20	-180	80
	-195	80

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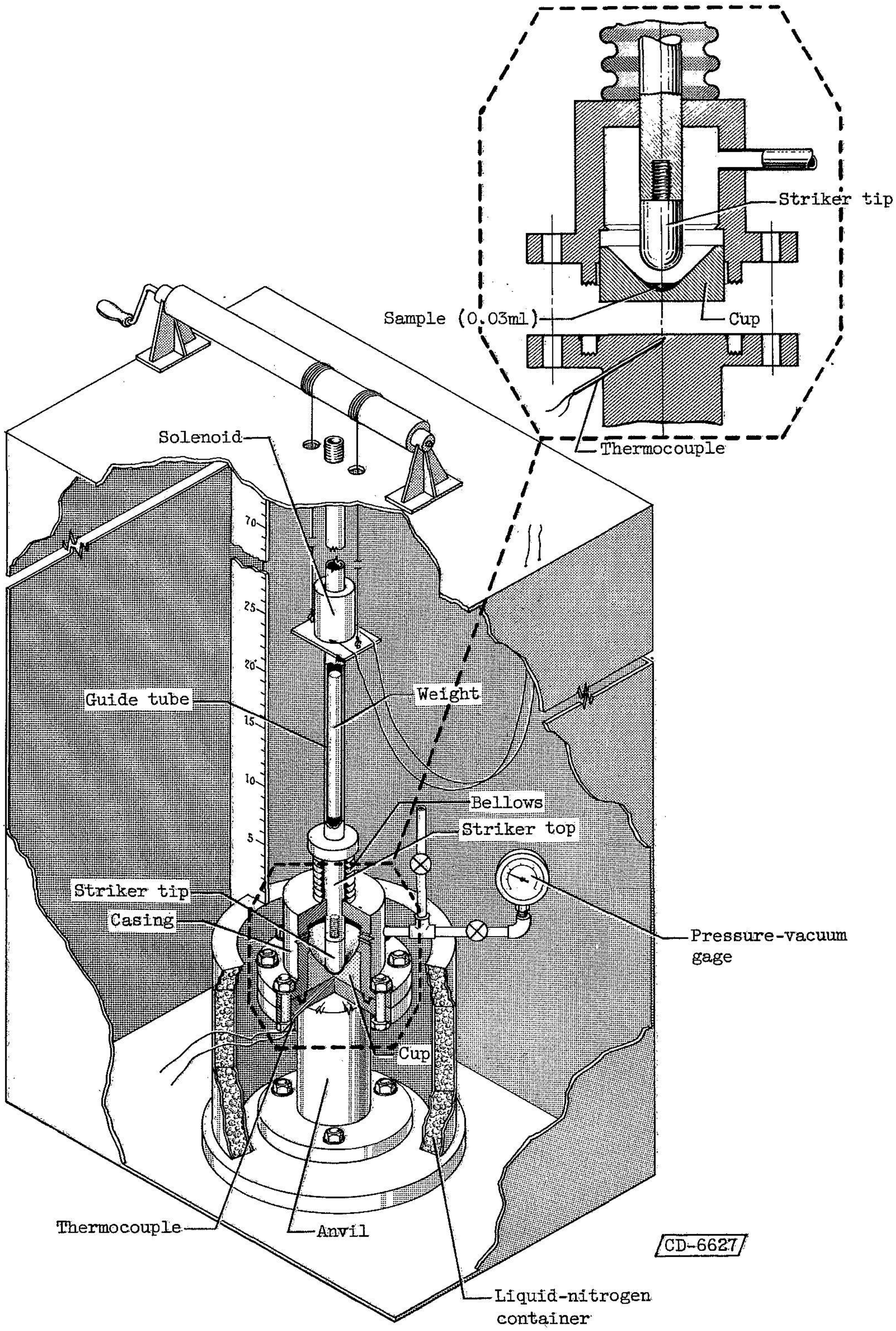

Figure 1. - Impact test apparatus.

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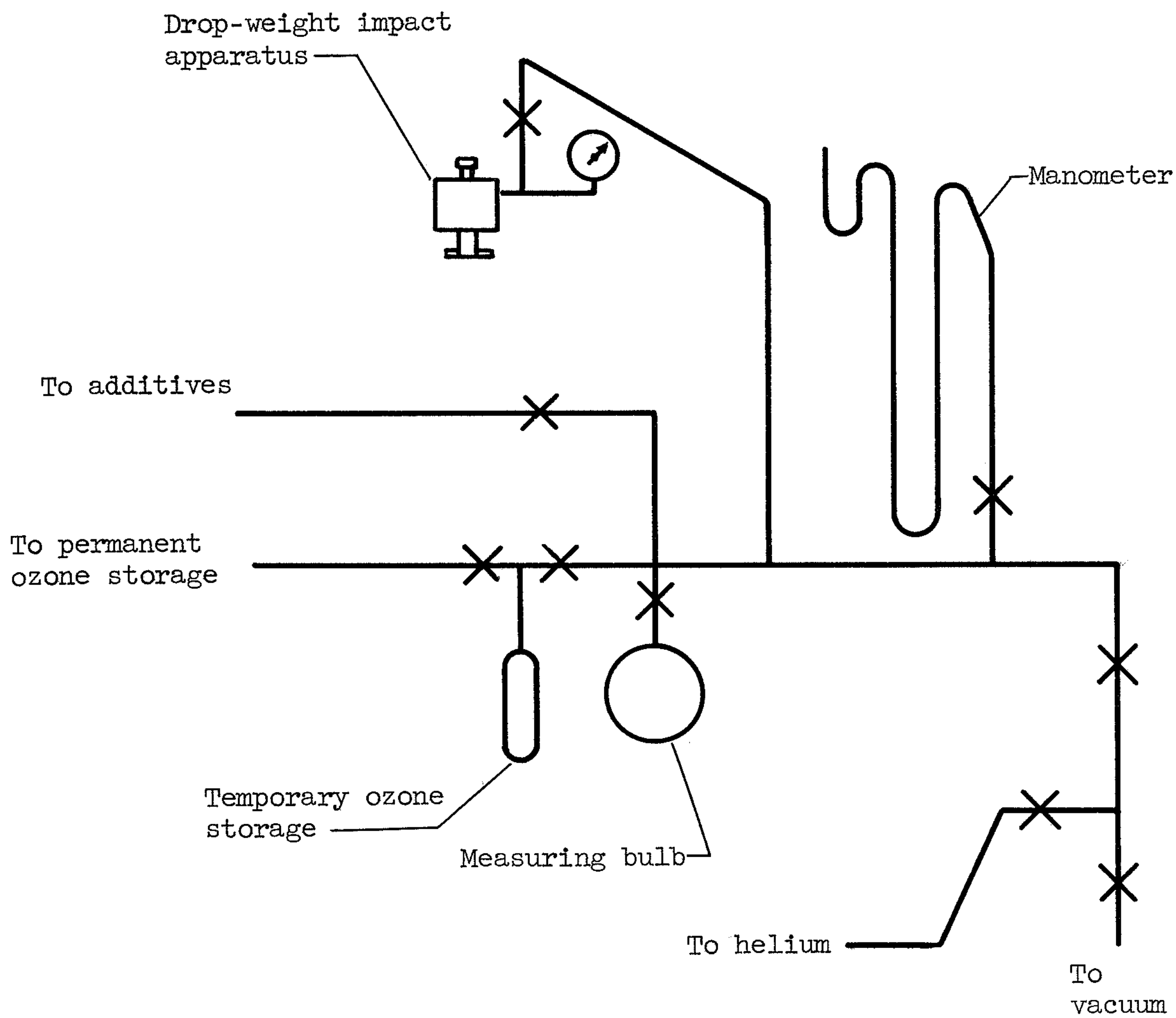

Figure 2. - Manifold.

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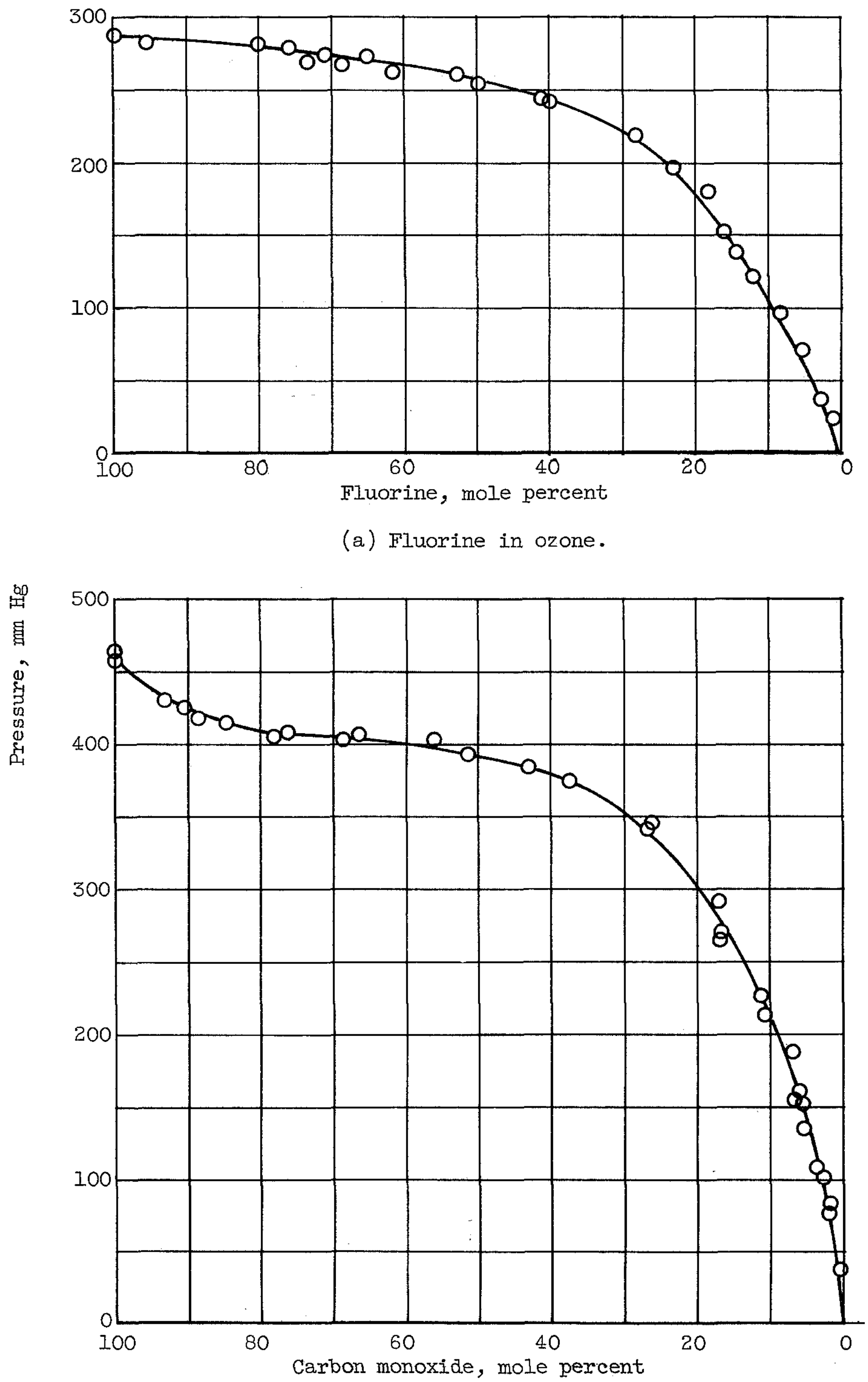

(a) Fluorine in ozone.

(b) Carbon monoxide in ozone.

Figure 3. - Vapor-pressure curves of ozone-fluorine and ozone - carbon monoxide mixtures at -195° C.

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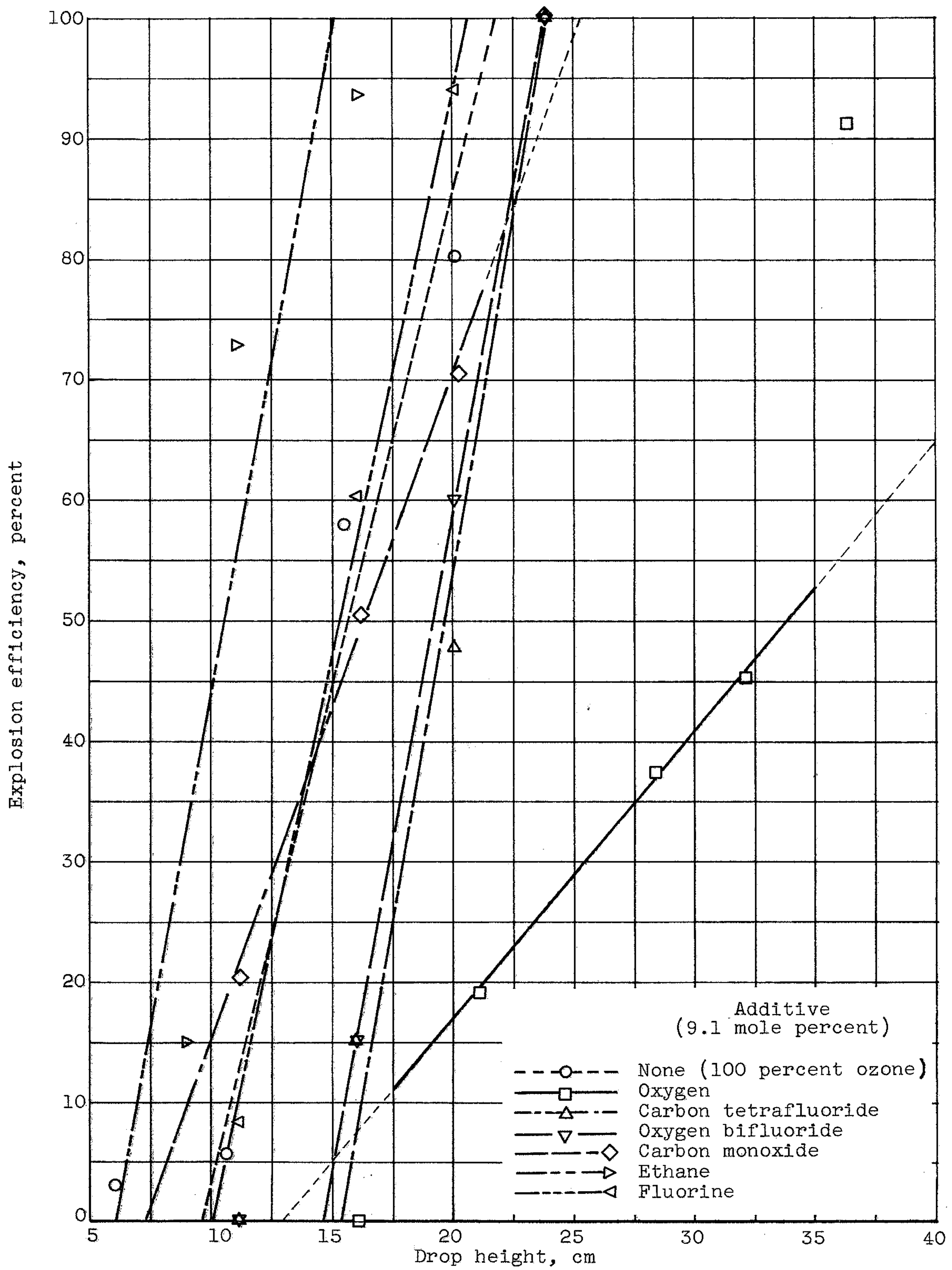

Figure 4. - Relation of explosion efficiency to drop height of ozone and ozone mixtures.

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